

Synthesis, Preparation, Properties And Applications of Nano Size Conducting Polymers And Blend

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ABSTRACT

Polyaniline-EB (Pani-EB), Polypyrrole(PPY), Acid doped Pani(Acid Pani) and Pani-EB/PPY blend were chemically synthesized and identified by FTIR. The nano size samples are prepared by casting technique and analysed by XRD. The dielectric studies have been carried out at different frequencies and temperatures with a view to study their effects on capacitance, dielectric constant and dielectric loss. The electrical conduction studies shows Acid Pani and PPY are having high conductivity than other nano size polymers. DC conduction studies reveals that Poole-Frenkel type of conduction is predominant in Pani-EB and Acid Pani. Also an account of the TEP and Hall studies on these samples were given in this paper. The fifth part describes the TSDC studies on these conducting polymer samples. From these studies, the relaxation time and E_g are also calculated. The pyroelectricity measurements on Pani-EB and lightly doped Pani films are also given reported. The sixth part deals with the breakdown properties of the above said conducting polymers. The thickness and temperature dependence of the breakdown field are investigated and suitable interpretations are given. The various breakdown patterns are photographed and presented in this part. The laser induced damage studies of the above said conducting polymer were reported.. The threshold damage and possible damage mechanisms and their dependence on thickness were examined.

INTRODUCTION

The advent of polymers represents one of the important industrial revolution of the twentieth century. Polymers with properties such as strength, toughness and frictional resistance often comparable with those of

metals and also offer very important advantages over the later viz, light weight, workability and economy have been developed. These materials not only replaced the metals in many areas of application but have also. infiltrated our day to-day life with wide range of products extending from most

common consumer goods to highly specialized applications in space and aeronautics. Interest in conductive organic polymers has considerably increased. These CP are classified as a new class of materials with great promise for a range of electronic devices. CP can be used as energy storage elements in capacitors and secondary batteries, as the semiconductor materials in Schottky diodes, insulated gate FET and LED and as a conductive layer for EMI and electrostatic protection [Halano *et al*, Huang *et al*, Kim *et al*, Lee *et al*, Halano *et al*, Wan.M *et al.*, Wan M.X *et al.*, Yu *et al.*]

EXPERIMENTS

Chemical synthesis method was employed for the polyaniline preparation. The product so obtained was the Polyaniline Emeraldine Base (Pani-EB) which was characterized and used for protonation. Pani-EB was doped with organic acid $\text{CH}_3\text{SO}_3\text{H}$. The doping level of the Pyrrole was varied by changing the Fe^{3+} / Pyrrole ratio. The polypyrrole (PPY) sample purity was examined by FTIR spectrum. Solution blending was carried out by dissolving the materials separately in the solvent. The two solutions were mixed well and was stirred for

one hour and then films were formed. Film casting technique was employed for the polymer film preparation. Vacuum evaporation technique was used for electrode deposition. Gravimetric and capacitance methods have been used to determine the thickness of polymer films and Rutherford Backscattering Spectrometry (RBS) technique was used to confirm the measured thickness of the polymer films.

RESULTS AND DISCUSSION

The defects present in the film represent a considerable departure from equilibrium. Application of mild heat treatment would anneal out these defects. Stabilization of these capacitors could also be achieved by repeated annealing cycles. The stability and reproducibility of the Pani-EB, Acid Pani, PPY and PPY/Pani-EB blend thin films have been achieved after two cycles of annealing with a duration of one hour each at 323 and 333 K respectively. All these films capacitance values were found to decrease with repeated annealing cycles. Stable value of capacitance were found to be achieved after two cycles of annealing. Annealing cycles for Pani-EB and PPY/Pani-EB as shown in Figure. 1 & 2.

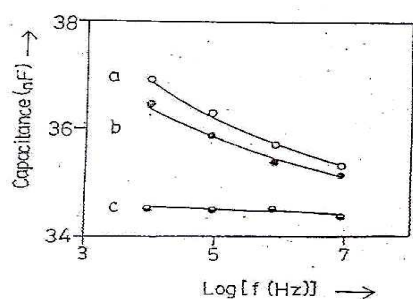


Figure.1. Annealing effect on capacitance of Pani – EB Films.

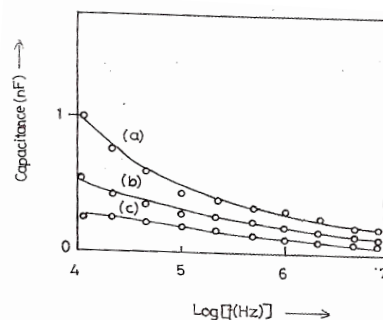


Figure.2. Annealing effect on capacitance of PPY/Pani – EB Films.

The dielectric behaviour of the polymer is determined by charge distribution and also statistical thermal motion of polar groups. The variation of capacitance with frequency in the range 10 k to 10 M Hz for different MPM capacitors are shown in Figure. 3 & 4.

Figure 3 shows the capacitance variation of the Pani-EB film. It is seen that for temperature below 383 K, the capacitance very gradually with increasing frequency (f). But at higher temperatures, the decrease in C with the increase of frequency is very predominant. The capacitance of the PPY/Pani-EB blend film shows an intermediate behaviour between the Pani-EB and PPY films as seen in Figure 4. The dielectric loss of all these above materials vary very similarly as the capacitance of these films. But in PPY films Figure 5 a completely different behaviour of the dielectric loss is observed. The dielectric loss initially decreases very slightly with increase of frequency and after 100 kHz, it increases predominantly with increasing frequency.

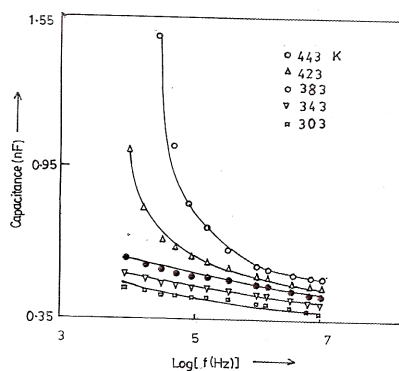


Figure 3. Capacitance versus frequency for Pani-EB film.

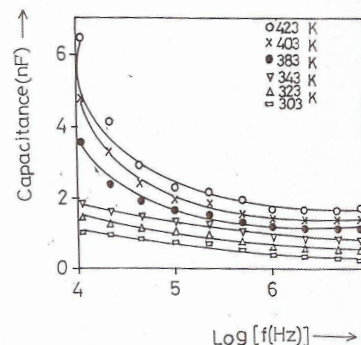


Figure 4. Capacitance versus frequency for PPY/Pani-EB blend film.

The variation of capacitance of the polymer films with temperature. Almost a completely temperature independent behaviour of the capacitance is observed for all the four polymer films at low frequencies. Only after at higher frequencies, the capacitance increases with the increase of temperature for Pani-EB, PPY, PPY/Pani-EB blend films. But in acid Pani films, no such increase is seen. The dielectric constant of these films behave very similarly as the capacitance of all these films.

Qualitatively the variation of capacitance and dielectric constants appear similar to those of other insulating materials. But quantitatively the data are quite different from those reported for any insulator. The origin of dielectric response of undoped and lightly doped polyaniline and polypyrrole are of interest especially in the context of the role of polaron and bipolaron defect state systems. Dielectric dispersion may be a bulk property of the polymers under study. These dielectric dispersion is not characterized by a single relaxation time exists in these films.

The variation of a.c. conductivity with frequency of Pani-EB films. It is seen that the slope of the curves decreases with the inverse

of temperature. Similar behaviour is observed for Acid Pani (Figure 6).

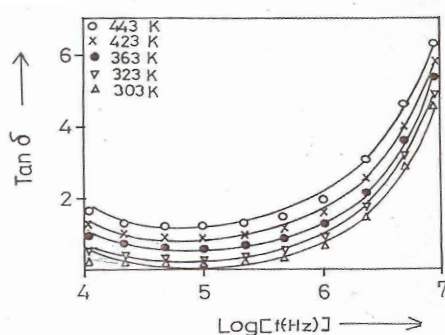


Figure 5. Variation of $\tan\delta$ with frequency of PPY film.

For PPy/Pani-EB blend films the slope of the curves is almost the same for all the temperatures. In PPY film also does not vary with the temperature. In all the films ac conductivity is found to vary according to the relation $\sigma \propto \omega^n$ where the value of n depends on the frequency. The value of n varies from 0.8 to 0.5 with the increase of temperature. The calculated activation energy values are given in the following table. The low value of activation energy confirms that the conduction is due to hopping of charge carriers like polarons and bipolarons [sakthivel *et al.*].

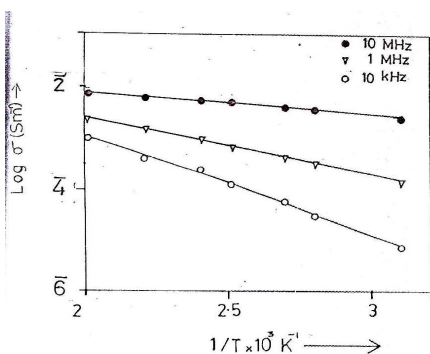


Figure 6. AC conductivity with $1/T$ for acid doped Pani Film

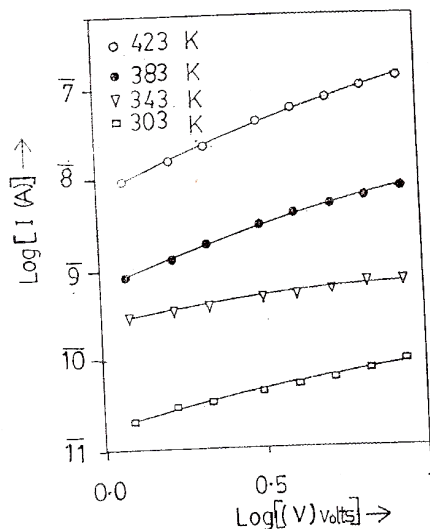


Figure 7. Double logarithmic plot of current versus voltage of Pani-EB films

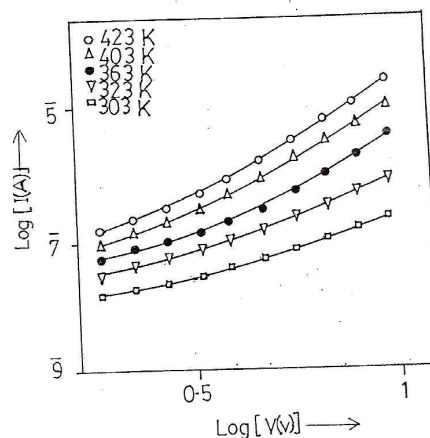


Figure 8. Double logarithmic plot of I versus V characteristics of Acid Pani films

Double logarithmic plot of current versus voltage characteristics of Pani-EB and Acid -Pani films are shown in Figure 7 & 8. It is seen that the current exhibits a voltage dependence of the form $I \propto V^n$, where n depends on the field region and temperature. The value of n varies from 1 to 1.6. In order to confirm the mechanism of conduction a plot

of $\log I$ versus $F^{1/2}$ is drawn Figure 9 & 10 which shows that Poole – Frenkel type of conduction mechanism is predominant.

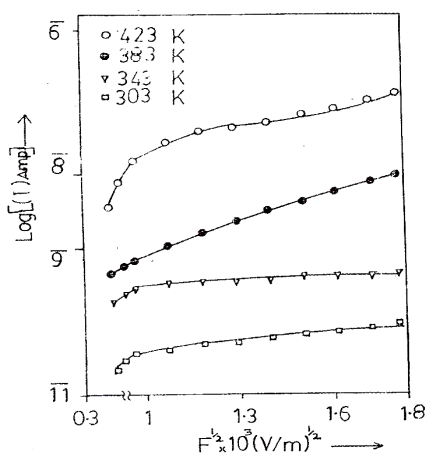


Figure 9. Change in current versus square root of field of Pani-EB film

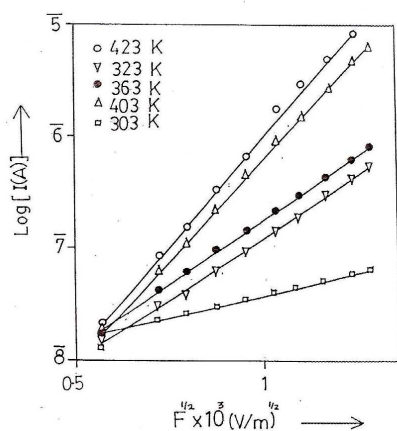


Figure 10. Change in current versus square root of field of Acid doped Pani film

Four probe studies indicate that polypyrrole (PPY) and Acid Pani films have high conductivity even at room temperature. For PPY film of thickness 0.1 micrometer, the

conductivity is found to be 200 S/cm. Hall studies show that the carrier concentration of PPY is higher than that of all the other polymers studied in the present work PPY and Acid Pani have p-type of charge carriers while Pani-EB has both p and n-type of charge carriers. The calculated values of carrier concentration, mobility, types of charge carriers are presented in Table 1. In order to understand the temperature behaviour of the conducting polymer system, the thermoelectric power measurements are carried out. In the case of PPY film, TEP with temperature shows the metallic behaviour for doped polypyrrole. The relatively small size of the TEP for these samples is a further evidence for their metallic character. The high value of TEP for PPY/Pani-EB blend is due to the influence of highly doped PPY on Pani-EB.

Table 1. Hall Parameters

Conducting polymer films	Carrier concentration (n)cm ³	Mobility cm ² /Vs	Type of charge carrier
1. PPY	1.1×10^{19}	9.72	p-type
2. Acid Pani	2.6×10^{17}	14.76	p-type
3. Pani-EB	3.8×10^{17}	-19.37	n-type
4. PPY/Pani-EB	4.1×10^{11}	1234	p-type
	7.5×10^8	-1958	n-type

The TEP studies indicate that the TEP that the TEP values of the polymer films increase with the increase of both temperature and thickness. The low TEP values observed for PPY films certify the metallic behaviour of these films. Thermally stimulated discharge current spectra of Pani-

EB and lightly doped polyaniline films at 333 K at different polarizing field are given in Figure 11 & 12.

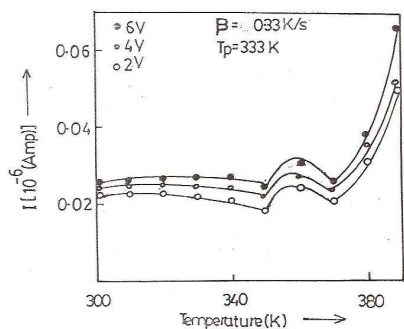


Figure 11. TSDC versus temperature of Pani-EB film polarized at 33K

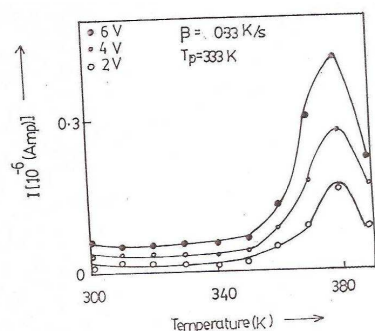
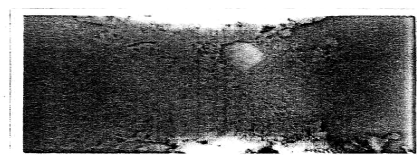


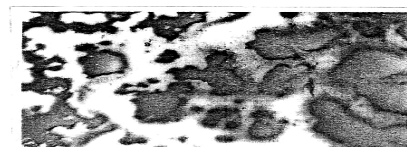
Figure 12. TSDC versus temperature of Acid Pani-EB film polarized at 333 K

Figure.13 a-d shows the complete breakdown patterns for pure Pani-EB and PPY films. Also it has been observed that the effect of breakdown is always greater at the edges inspite of the reinforcement of insulating layer. When the laser beam passes through the film according to the energy of the pulses, different damage patterns were observed in the films. The damage sites observed in Pani-EB, Acid Pani, PPY and PPY/Pani-EB blend films

are shown in Figure 14 a-d. Laser damage studies on these films show that Pani-EB films are having higher threshold energy density than other polymer films.



(a)



(b)



(c)



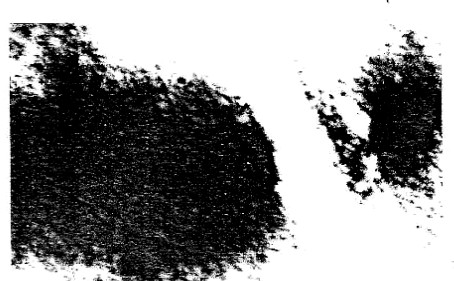
(d)

Figure 13 a-d Breakdown patterns for pure Pani-EB, PPY, PPY and PPY/Pani-EB b films.

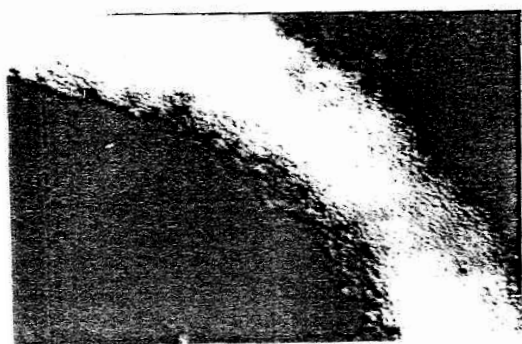
For Acid Pani films of thicknesses ranging from 3 to 30 micrometer the threshold energy density varies from 120 to 220 m J cm⁻²



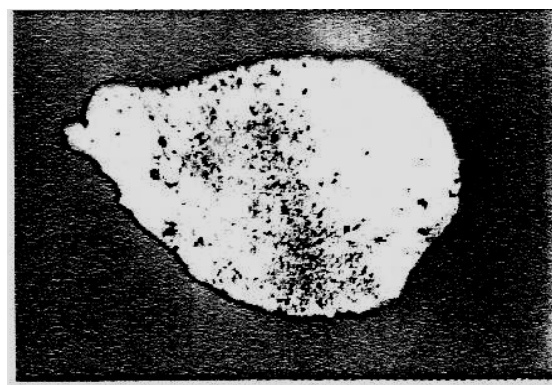
(a)



(d)



(b)



(c)

Figure 14 a-d Laser damage sites in Pani EB, Acid Pani, PPY and PPY/Pani-EB films

Using the above said conducting polymer films, sensor and Schottky diode have been fabricated. The behaviour of these sensors on the exposure to acetone and methanol atmosphere is studied. From the observations, it is seen that the sensing behaviour of polyaniline-EB and polypyrrole films are good with a quick recovery for acetone and methanol gases respectively. In the case of schottky barrier diode, it is found that the junction characteristics is mainly controlled by the carrier concentrations. The application oriented study of these polymer materials prove that these materials possess high potentiality to find suitable place in many electronic gadgets, gas sensors and thermal detectors. It is belived that the data presented in this paper, along with the other data available in the literatures, will be very much useful for the exploitation of these films in a variety of applications [sakthivel *et al*, Zhang *et al*, Pillalamarri *et al*].

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